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High Temperature X-Ray Study of the Thermal Expansion of Pd_9Se_8 and Rh_9S_8

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Pd_9Se_8 and Rh_9S_8 with cubic crystal symmetry, have been studied by the X-ray powder method at temperatures in the range from 20 to 940°C. The average linear thermal expansion coefficient, β_a, is equal to 9.8×10^{-6} °C^{-1} for Pd_9Se_8 (20–625°C), 9.3×10^{-6} °C^{-1} for Rh_9S_8 (20–300°C) and 7.4×10^{-6} °C^{-1} for Rh_9S_8 (428–866°C). The volume expansion coefficient, a, is 29.5×10^{-6} °C^{-1} for Pd_9Se_8 (20–625°C), 27.8×10^{-6} °C^{-1} for Rh_9S_8 (20–300°C) and 22.2×10^{-6} °C^{-1} for Rh_9S_8 (428–866°C).

In a recent study of the thermal expansion of PtS_2, $PtSe_2$, $PtTe_2$ and $PdTe_2$, all with structures of the $Cd(OH)_2$-type, Kjekshus and Grønvold [1] found a general departure from linearity in the expansion perpendicular to the layers at higher temperatures. Since the reasons for the different modes of thermal expansion at higher temperatures are not fully explained by the existing theories for the perfect lattice, further experimental data might be desirable before a theoretical explanation is proposed.

The present paper is concerned with the thermal expansion of Pd_9Se_8 [2] and Rh_9S_8 [3], which have cubic symmetry and are probably isostructural. These compounds were also chosen in order to check the accuracy of the X-ray method for thermal expansion studies of compounds with relatively long cell edges of about 10 Å. The fact that the positions of the atoms in the unit cell are not known is of secondary importance, since the thermal expansion of the interatomic distances is equal to the expansion of the cell edges.

EXPERIMENTAL

Pd_9Se_8 was prepared [2] by heating a mixture of $PdSe_{1.00}$ and palladium, corresponding to the formula Pd_9Se_8, in an evacuated and sealed silica tube for 10 days at 650°C and 50 days at 450°C. Rh_9S_8 was prepared [3] by heating rhodium and sulfur in the right proportions in an evacuated, sealed silica tube for 14 days at 690°C and another 14 days at 350°C. Both samples were finally slowly cooled to room temperature.

Information about the purity of the elements is given elsewhere [2,3].

Table 1. Lattice constants and unit cell volumes for Pd_9Se_8 at different temperatures.

t(°C)	a(Å)	V(Å^3)
20	10.6060	1193.04
155	10.6200	1197.77
220	10.6268	1200.07
330	10.6382	1203.94
402	10.6457	1206.49
531	10.6595	1211.18
625	10.6694	1214.51
650	10.6725	1215.62

X-Ray powder photographs of the compounds were taken in a 190 mm Unicam high-temperature camera, with the samples sealed in thin-walled quartz capillaries. Pd_9Se_8 was studied at temperatures between 20 and 650°C. The highest temperature is close to the melting point of 665 ± 15°C. Rh_9S_8 was studied at temperatures between 20 and 940°C.

By means of a voltage regulator, the registered temperature of the furnace surrounding the specimen was kept constant within ± 5°C. The Pt/Pt-Rh thermocouples of the furnace had been calibrated with a standard couple located at the position of the specimen. Lattice constants are given i Ångström units ($\lambda_{CuK\alpha_1}$ = 1.54050 Å). Only the high-angle reflections of the diffraction pattern were used in the calculation of the lattice constants. The lattice constants were found by extrapolation according to the method given by Nelson and Riley [4]. The probable error in the lattice constant determinations at temperatures above room temperature was estimated to be about 0.01 %. This included a possible error due to variation in the composition of the sample with temperature. A much better reproducibility of about 0.003 % is found, however, between the results for two different expansion runs. Errors due to specimen contamination can be neglected, since the lattice constants at room temperature before and after the high temperature treatment were equal within the limits of the experimental error.

RESULTS

The results of the lattice constant measurements are listed in Tables 1 and 2. Here are also listed the unit cell volumes. The ratios $\frac{a_t - a_{20}}{a_{20}} = \frac{\Delta a}{a_{20}}$

Table 2. Lattice constants and unit cell volumes for Rh_9S_8 at different temperatures.

t(°C)	a(Å)	V(Å^3)
20	9.9116	973.71
120	9.9204	976.31
208	9.9289	978.82
300	9.9383	981.60
428	9.9495	984.93
538	9.9576	987.33
615	9.9632	989.00
681	9.9683	990.52
766	9.9744	992.34
866	9.9818	994.55
940	9.9894	996.52

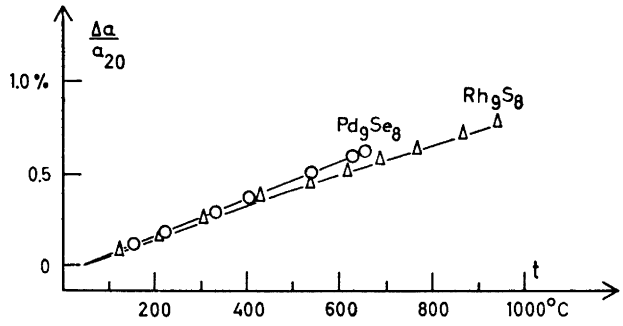

Fig. 1. Relative lattice constant variation as function of temperature.

and $\frac{V_t - V_{20}}{V_{20}} = \frac{\Delta V}{V_{20}}$ are calculated and plotted as $\frac{\Delta a}{a_{20}}$ *versus* t, and $\frac{\Delta V}{V_{20}}$ *versus* t, respectively. The calculations of the expansion coefficients were based upon these data.

The change in the length of the a-axis is similar below about 300°C for both Pd_9Se_8 and Rh_9S_8. As shown in Fig. 1, the a-axis increases linearly with increasing temperature. The expansion coefficient β_a is equal to 9.8×10^{-6} $°C^{-1}$ for Pd_9Se_8 (20—625°C) and 9.3×10^{-6} $°C^{-1}$ for Rh_9S_8 (20—300°C). At temperatures between 428 and 866°C the a-axis of Rh_9S_8 increases more slowly

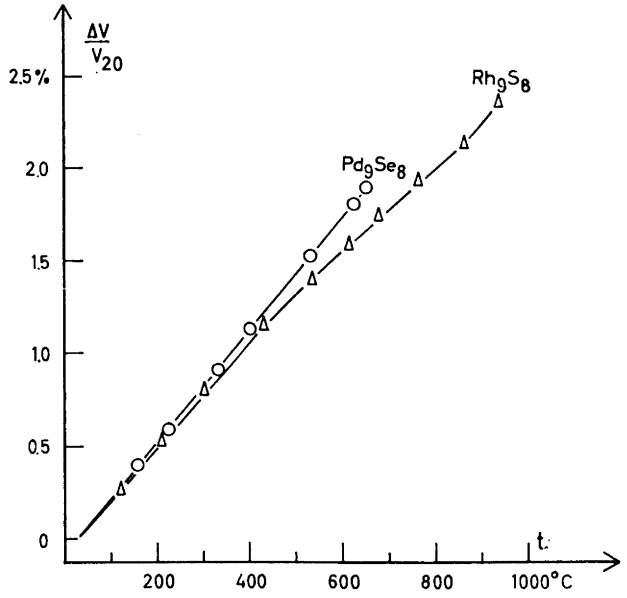

Fig. 2. Relative changes in volume with temperature.

than at lower temperatures. The thermal expansion is approximately linear, with expansion coefficient β_a equal to 7.4×10^{-6} °C^{-1} for Rh_9S_8 (428—866°C).

The volume expansion is plotted as function of the temperature in Fig. 2. For both compounds the volume expansion has a similar temperature dependence as the a-axis. Since β_a is of the order 10^{-5}, the average thermal volume expansion coefficient α is approximately $3\beta_a$. The numerical values for α are 29.5×10^{-6} °C^{-1} for Pd_9Se_8 (20—625°C), 27.8×10^{-6} °C^{-1} for Rh_9S_8 (20—300°C) and 22.2×10^{-6} °C^{-1} for Rh_9S_8 (428—866°C).

The intensities of the reflections on X-ray photographs taken at higher temperatures are almost equal to those of the corresponding photographs taken at room temperature. The parameters must thus be nearly the same. Because of the cubic symmetry the thermal expansion of the interatomic distances is approximately equal to the expansion of the a-axis (*cf.* Fig. 1).

The obtained expansion curves for Pd_9Se_9 deviate little from linearity. The assumed large increase [5,6] in the coefficient of thermal expansion in the temperature region just below melting does not occur. As the a-axis and the volume of Rh_9S_8 increase more slowly above 428°C than at lower temperatures, the relative expansion is still on the upper part of the sigmoidal curve. The values for the a-axis at 940°C (*cf.* Table 1) indicate that a more rapid increase might well take place above this temperature.

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